

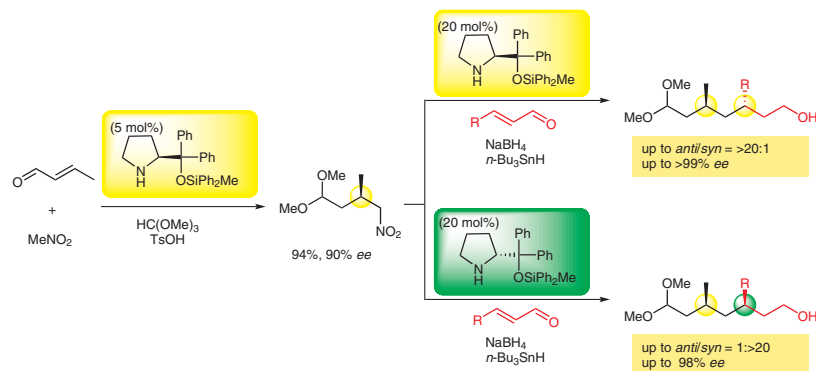
# Asymmetric Synthesis of Chiral 1,3-Dimethyl Units Through a Double Michael Reaction of Nitromethane and Crotonaldehyde Catalyzed by Diphenylprolinol Silyl Ether

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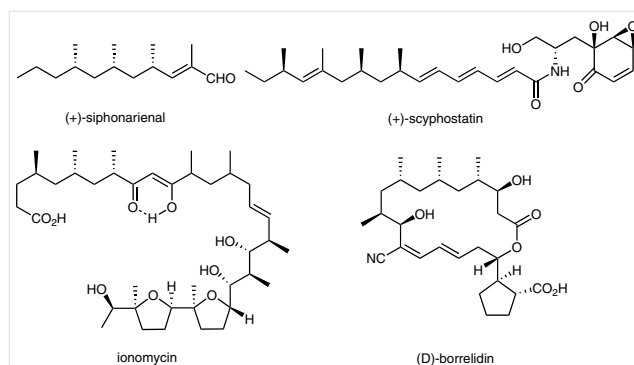
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**Abstract** An efficient synthetic route to install chiral 1,3-dimethyl units through a double Michael reaction of crotonaldehyde and nitromethane catalyzed by diphenylprolinol silyl ether is developed. Either 1,3-*syn*- or 1,3-*anti*-dimethyl units are obtained selectively depending on the enantiomer of the diphenylprolinol silyl ether catalyst used. The side chain of pneumocandin B<sub>0</sub> is synthesized enantioselectively by using the present method as a key step.

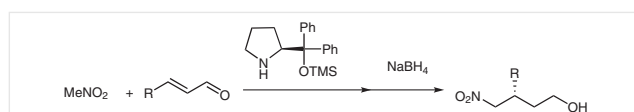
**Key words** organocatalyst, Michael reaction, asymmetric synthesis, diastereoselective reaction, diphenylprolinol silyl ether



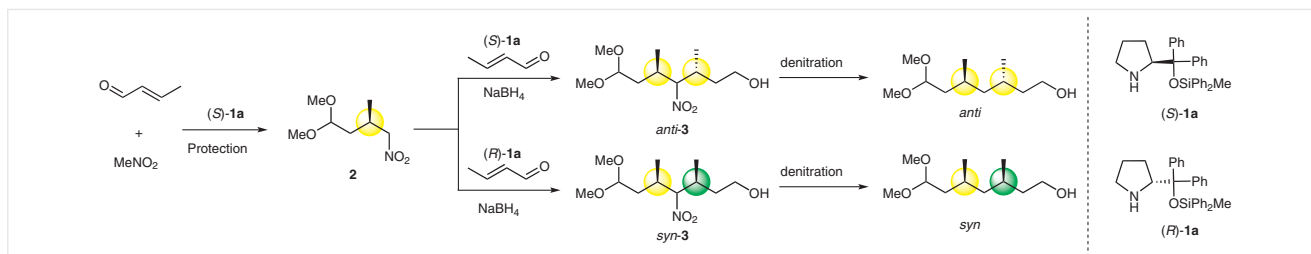
**Figure 1** Natural products with a 1,3-dimethyl unit

The 1,3-dimethyl unit is found in many natural products, including siphonarional,<sup>1</sup> ionomycin,<sup>2</sup> scyphostatin,<sup>3</sup> and borrelidin (Figure 1),<sup>4</sup> and the stereoselective synthesis of chiral 1,3-dimethyl units is considered an important synthetic topic.<sup>5</sup> There are many methods available for the diastereo- and enantioselective synthesis of *anti*- and *syn*-1,3-dimethyl units. The iterative Michael reaction of methyl groups under reagent control is a widely employed method,<sup>6</sup> and iterative allylic substitution and alkylation of chiral enolates is also used.<sup>7</sup> Negishi's Zr-catalyzed carboalumination (ZACA) reaction is a powerful method for the preparation of 1,3-dimethyl units,<sup>8</sup> and Aggarwal recently reported an assembly-line synthesis that proceeds through iterative homologation of boronic esters with chiral lithiated benzoate esters and chloromethyl lithium.<sup>9</sup> Some of the methods use asymmetric catalytic reactions.<sup>6,8</sup> In spite of these elegant methods, a procedure which is suitable for the large-scale preparation of 1,3-dimethyl units is needed.

We have already reported the asymmetric Michael reaction of an  $\alpha,\beta$ -unsaturated aldehyde with nitromethane catalyzed by a diphenylprolinol silyl ether<sup>10</sup> as an effective organocatalyst (Scheme 1).<sup>11</sup> The sequential use of this Michael reaction would afford either the *syn*- or *anti*-1,3-dimethyl unit stereoselectively (Scheme 2). The Michael reaction of nitromethane and crotonaldehyde catalyzed by (*S*)-diphenylprolinol silyl ether (*S*)-**1a**,<sup>12</sup> followed by acetalization would provide **2**. A second Michael reaction of the generated nitroalkane **2** and crotonaldehyde, catalyzed by either (*S*)- or (*R*)-diphenylprolinol silyl ether, would then afford the desired *anti*- or *syn*-1,3-dimethyl unit, respectively. The realization of this scenario is described herein.

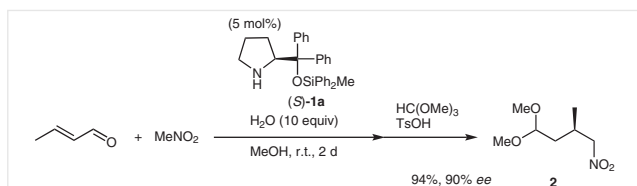


**Scheme 1** An asymmetric Michael reaction catalyzed by a diphenylprolinol silyl ether



**Scheme 2** The idea for the synthesis of *anti*- and *syn*-dimethyl units

The first Michael reaction of crotonaldehyde and nitromethane was carried out using 5 mol% of (*S*)-diphenylprolinol diphenylmethylsilyl ether (*S*)-**1a**<sup>12</sup> as the catalyst in MeOH in the presence of 10 equivalents of H<sub>2</sub>O to afford the Michael product, which was treated with HC(OMe)<sub>3</sub> and a catalytic amount of TsOH in the same vessel to provide nitroacetal **2** in 94% yield and 90% ee (Scheme 3). This reaction required four days to reach completion when THF was employed as the solvent, as described previously,<sup>13</sup> but was complete within two days in MeOH and proceeded with excellent enantioselectivity.



**Scheme 3** The initial Michael reaction of crotonaldehyde and nitromethane

The second Michael reaction of **2** and crotonaldehyde was then investigated using diphenylprolinol trimethylsilyl ether (*S*)-**1b** as the catalyst (Table 1). Alcohol **3** was obtained in 43% yield as a diastereomeric mixture after treatment of the Michael product with NaBH<sub>4</sub> (entry 1). To improve this yield, the reaction conditions were screened.

For the Michael reaction of a nitroalkane and an  $\alpha,\beta$ -unsaturated aldehyde, we have previously reported several reaction conditions. (1) For  $\beta$ -aryl  $\alpha,\beta$ -unsaturated aldehydes, the solvent was MeOH with an acid additive.<sup>11a</sup> (2) For  $\beta$ -alkyl  $\alpha,\beta$ -unsaturated aldehydes, the solvent was MeOH without an acid additive.<sup>11a</sup> (3) For  $\beta,\beta$ -disubstituted  $\alpha,\beta$ -unsaturated aldehydes, neat conditions were employed without an acid additive.<sup>11b</sup> Other research groups have reported alternative reaction conditions: in the reaction of a  $\beta$ -aryl  $\alpha,\beta$ -unsaturated aldehyde, the Merck group reported the use of aqueous THF in the presence of pivalic acid and B(OH)<sub>3</sub>,<sup>14</sup> whereas Wang and co-workers used EtOH with benzoic acid as an acid additive.<sup>15</sup>

When the reaction was conducted in MeOH with 10 equivalents of water, the product was obtained in 43% yield after 7.5 hours (Table 1, entry 1); no reaction occurred without water (entry 2). Addition of an acid was not effective

in the present reaction (entry 3). The use of either THF or neat conditions were also not suitable (entries 4–7). In these reactions, nitroalkane **2** was recovered in good yield,<sup>16</sup> while crotonaldehyde was consumed. One of the side products of crotonaldehyde was found to be the self-aldol product, presumably formed via the dienamine intermediate generated from crotonaldehyde and the catalyst. To suppress this side reaction, crotonaldehyde was added slowly. However, the desired reaction did not occur because of a further side reaction involving the formation of 1-methoxybut-2-en-1-ol, which would be generated by the reaction of MeOH and crotonaldehyde (entry 8). To also suppress this side reaction, slow addition of a solution of crotonaldehyde in THF was examined, which afforded the desired product in 62% yield (entry 9).<sup>17</sup>

**Table 1** The Effect of Solvent, Additive and Addition Time on the Asymmetric Michael Reaction of Nitroalkane **2** and Crotonaldehyde<sup>a</sup>

Entry	Solvent	H <sub>2</sub> O (equiv) <sup>b</sup>	Time (h)	Yield (%) <sup>c</sup>
1	MeOH	10	7.5	43
2	MeOH	0	7.5	<5
3 <sup>d</sup>	MeOH	10	2	<5
4	THF	10	28	<5
5	THF	0	28	<5
6	neat	10	28	<5
7	neat	0	28	<5
8 <sup>e</sup>	MeOH	10	11	<5
9 <sup>f</sup>	MeOH	10	11	62

<sup>a</sup> Unless noted otherwise, the reaction was performed by employing **2** (0.6 mmol), crotonaldehyde (1.2 mmol), and (*S*)-**1b** (0.12 mmol) in solvent (1.2 mL) with H<sub>2</sub>O (6.0 mmol) (or without H<sub>2</sub>O) at room temperature for the indicated time.

<sup>b</sup> Amount of water.

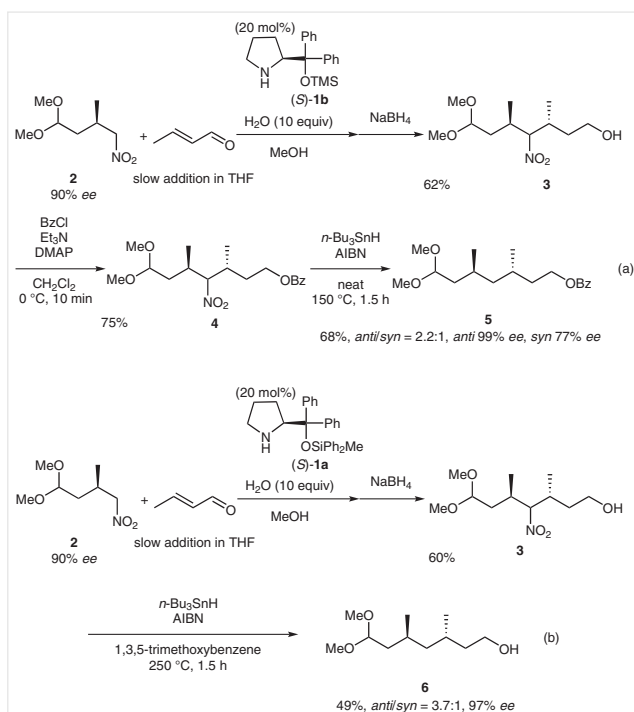
<sup>c</sup> Yield of purified product.

<sup>d</sup> Benzoic acid (20 mol%) was added.

<sup>e</sup> A MeOH solution of crotonaldehyde was added over 10 h.

<sup>f</sup> A THF solution of crotonaldehyde was added over 10 h.

The product, which contains three chiral centers, was obtained as a mixture of several diastereomers. Denitration was then investigated. Alcohol **3** was converted into its benzoyl ester **4**. After optimization of the denitration conditions, it was found that the reaction of **4** with  $n\text{-Bu}_3\text{SnH}$  proceeded at  $150\text{ }^\circ\text{C}$  to afford alcohol **5** in 68% yield with 2.2:1 diastereoselectivity (Scheme 4a).<sup>18,19</sup> To increase the diastereoselectivity, we further optimized the second Michael reaction using an organocatalyst with a different silyl substituent. An improved result was obtained when diphenylmethylsilyl ether (*S*)-**1a**<sup>12</sup> was employed instead of trimethylsilyl ether (*S*)-**1b** to provide, after denitration, the product **6** with 3.7:1 diastereoselectivity (Scheme 4b). As we found that protection of the hydroxy moiety was not necessary during our investigation of the denitration, we converted **3** into alcohol **6** according to the method shown in Scheme 4b. Although the diastereoselectivity was moderate, excellent enantioselectivity was obtained (97% *ee*). It is noteworthy that the enantioselectivity increased from 90% to 97% (*vide infra*).

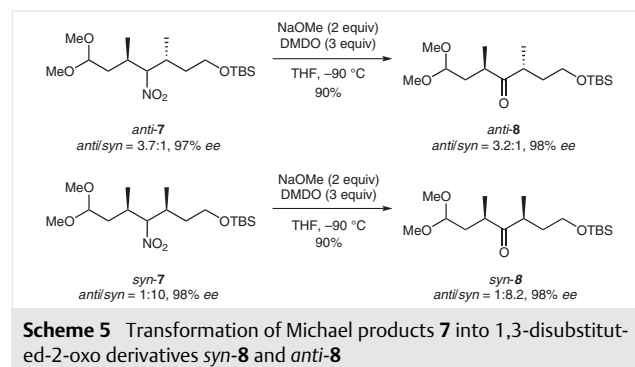


**Scheme 4** (a) Denitration of alcohol **3**. (b) Optimized conditions for the second Michael reaction and subsequent denitration

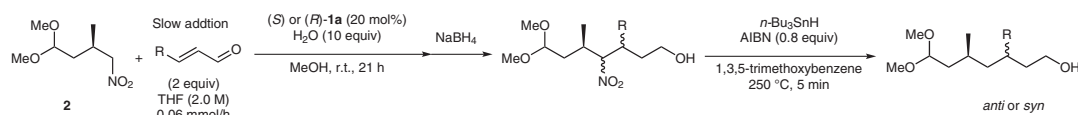
Next, the generality of the asymmetric double Michael reaction was investigated (Table 2). Although the *anti*-1,3-dimethyl substituent was obtained with moderate diastereoselectivity, excellent enantioselectivity was generated (entry 1). Both the 1,3-*syn*-dimethyl isomer and the 1,3-*syn*-methyl ethyl isomer were obtained with excellent diastereoselectivities and enantioselectivities (entries 2 and 3).

In the second Michael reaction, cinnamaldehyde was also a suitable Michael acceptor, affording the *syn*- and *anti*-isomers with excellent stereoselectivity (entries 4 and 5). 3-Aryl-substituted propenals could also be successfully employed. Notably, both an electron-deficient aryl, such as that with a *p*-trifluoromethylphenyl substituent, and an electron-rich aryl, such as that with a *p*-methoxyphenyl substituent, were suitable substrates (entries 6 and 7). Table 2 indicates that the diastereoselectivities are moderate to good and that they depend on the substituents. However, the enantioselectivities of the final products are found to be excellent (>95% *ee*) for both 1,3-*anti*- and 1,3-*syn*-isomers. It should be noted that the enantioselectivity increased in all the cases, although that of the first Michael product **2** was 90%.

The double Michael product could also be transformed into the 1,3-disubstituted-2-oxo derivative through a Nef reaction.<sup>20</sup> When *anti*-**7** and *syn*-**7** were treated with NaOMe and dimethyldioxirane (DMDO),<sup>20a</sup> 1,3-*anti*- and 1,3-*syn*-dimethylketones (*anti*-**8** and *syn*-**8**), respectively, were obtained in good yields, albeit with a slight decrease of the diastereoselectivity and enantioselectivity (Scheme 5).



Although the enantiomeric excess of the first Michael product was 90%, the double Michael product was formed with an excellent enantioselectivity that was much higher than that of the first Michael reaction. The origin of this enhanced enantioselectivity can be explained as follows (Scheme 6). In the first Michael reaction, **2** and *ent*-**2** were generated in a 95:5 ratio, in which **2** was formed predominantly rather than *ent*-**2**. When **2** reacted with crotonaldehyde catalyzed by (*S*)-**1a**, in which the (*R*)-isomer of the newly generated methyl group would be predominantly generated,<sup>11</sup> *anti*-**3** was formed predominantly, while the generation of (*S*)-isomers such as *syn*-**3** and *anti-ent*-**3** would be minor. As *ent*-**2** is generated in a small amount in the first reaction and the generation of *anti-ent*-**3** is also a minor reaction path in the second Michael reaction, the amount of *anti-ent*-**3** would be very little. If the stereoselec-

**Table 2** The Two-Pot Synthesis of 1,3-Disubstituted Alkanols<sup>a</sup>

Entry	Product	Cat.	Michael reaction yield (%) <sup>b</sup>	dr <sup>c</sup>	Denitration yield (%) <sup>b</sup>	anti/syn <sup>d</sup>	ee <sup>d</sup>
1		S	60	nd	49	3.7:1	97
2		R	63	nd	51	1:10	98
3 <sup>e</sup>		R	60	nd	44	1:>20	97
4		S	80	63:28:7:2	54	13:1	98
5		R	78	59:30:6:5	48	1:15	96
6		S	91	53:42:5:0	62	>20:1	>99
7		S	80	62:26:9:3	65	5.9:1	99

<sup>a</sup> First step (Michael reaction): Unless noted otherwise, the reactions were performed by employing **2** (0.6 mmol),  $\alpha,\beta$ -unsaturated aldehyde (1.2 mmol), (S)-**1a** or (R)-**1a** (0.12 mmol), and H<sub>2</sub>O (6.0 mmol) in MeOH (1.2 mL) at room temperature via slow addition of the aldehyde over 20 h and further stirring of the reaction mixture for 1 h. Second step (denitration reaction): Unless noted otherwise, the reactions were performed by employing the Michael adduct (0.4 mmol), *n*-Bu<sub>3</sub>SnH (2.0 mmol), AIBN (0.32 mmol), and 1,3,5-trimethoxybenzene (14.0 mmol) at 250 °C for 5 min.

<sup>b</sup> Yield of purified product.

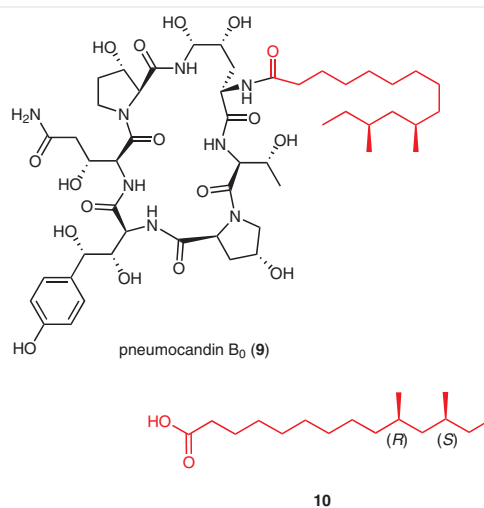
<sup>c</sup> dr = diastereomer ratio in the Michael reaction determined by <sup>1</sup>H NMR spectroscopy; nd = not determined.

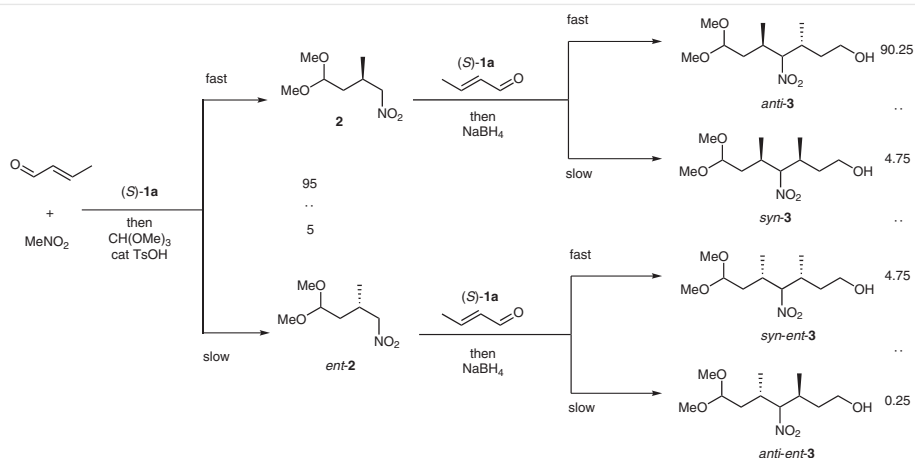
<sup>d</sup> Diastereomer ratio and enantiomeric excess were determined by HPLC analysis on a chiral column.

<sup>e</sup> Slow addition over 40 h during the Michael reaction.

tivity of the newly generated stereocenter in the second Michael reaction is 95:5, the ratio of *anti-3* and *anti-ent-3* would be 90.25:0.25. Thus, the ee in the final product **3** is much higher than that of the first Michael product **2**.

The present method was applied to the asymmetric synthesis of the side chain of pneumocandin B<sub>0</sub> (**9**) (Figure 2).<sup>21</sup> Pneumocandin B<sub>0</sub> was isolated from the fermentation broth of the fungus *Glarea lozoyensis* by Merck & Co. Its fungal-specific mode of action is inhibition of the biosynthesis of  $\beta$ -(1,3)-D-glucan, which is an essential cell wall component of many pathogenic fungi. The stereoselective synthesis of the (10*R*,12*S*)-dimethylmyristoyl side chain **10** of this compound through the use of Enders' RAMP method and diastereoselective alkylation of the chiral enolate has previously been reported.<sup>21c</sup>

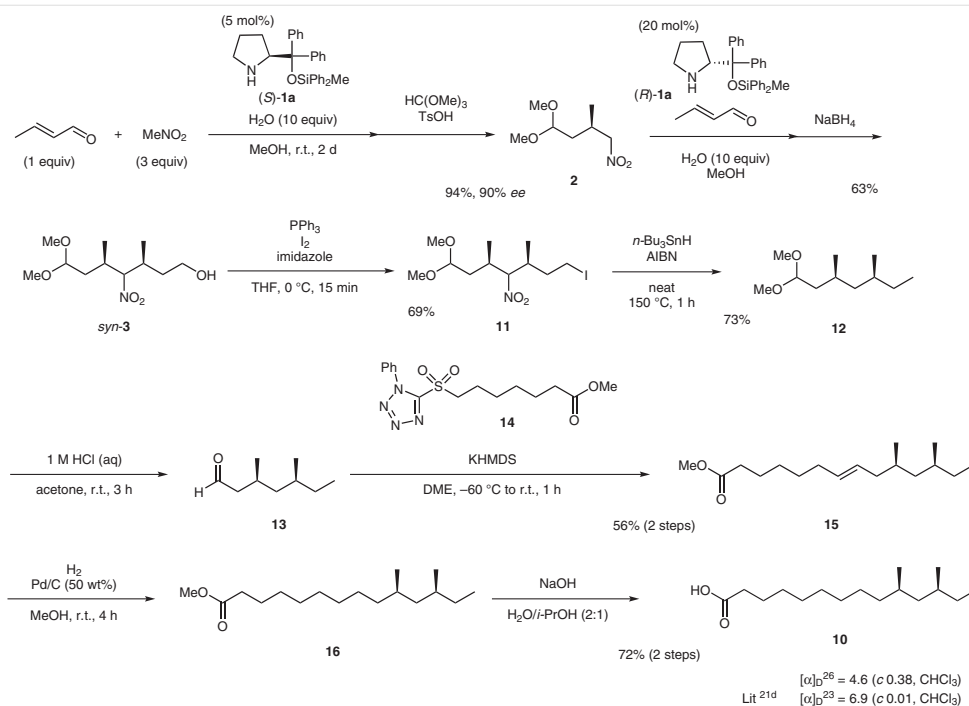
**Figure 2** The structure of pneumocandin B<sub>0</sub> (**9**) and its side chain **10**



**Scheme 6** The reason for the higher ee of the second Michael product

Our synthesis of the side chain **10** started with the Michael reaction of nitromethane and crotonaldehyde catalyzed by diphenylprolinol silyl ether (*S*)-**1a**. Subsequent acetalization provided **2** in 94% yield with 90% ee. The second Michael reaction with crotonaldehyde proceeded in the presence of (*R*)-**1a**, followed by treatment with NaBH<sub>4</sub> to afford alcohol *syn*-**3** in 63% yield. The enantioselectivity of *syn*-**3** is 98%, which was determined after denitration (see Table 2, entry 2). Alcohol *syn*-**3** was converted into haloalkane **11** in 69% yield by reaction with Ph<sub>3</sub>P and I<sub>2</sub>.<sup>22</sup> Dehalogenation and denitration occurred in the same pot<sup>23</sup> by

treatment with *n*-Bu<sub>3</sub>SnH and AIBN at 150 °C<sup>18</sup> to afford acetal **12** in 73% yield. Treatment of acetal **12** with aqueous HCl gave aldehyde **13**, which was used in the next step without purification. The Julia–Kocienski reaction with **14** proceeded smoothly to afford (*E*)-alkene **15** in 56% yield over two steps.<sup>24</sup> Hydrogenation followed by hydrolysis using aqueous NaOH afforded the side chain of pneumocandin B<sub>0</sub> **10** in 72% yield over two steps (Scheme 7). The physical properties of synthetic **10** were identical in all respects to the reported data.<sup>21d</sup>



**Scheme 7** Synthesis of the side chain of pneumocandin B<sub>0</sub>

In conclusion, we have developed an efficient method for the synthesis of chiral 1,3-dimethyl units through a double Michael reaction of an aldehyde and nitroalkane catalyzed by a diphenylprolinol silyl ether. There are several noteworthy features of this reaction. Either 1,3-*syn*- or 1,3-*anti*-dimethyl units can be selectively synthesized depending on the appropriate choice of enantiomer of the diphenylprolinol silyl ether catalyst. The excellent optical purity of the double Michael product was much higher than that of the first Michael reaction because of the 'meso-trick'. In addition to the 1,3-dimethyl unit, both 1,3-methyl alkyl and 1,3-methyl aryl units can be prepared. Finally, the side chain of pneumocandin B<sub>0</sub> was enantioselectively synthesized by using the present method as a key step.

### Funding Information

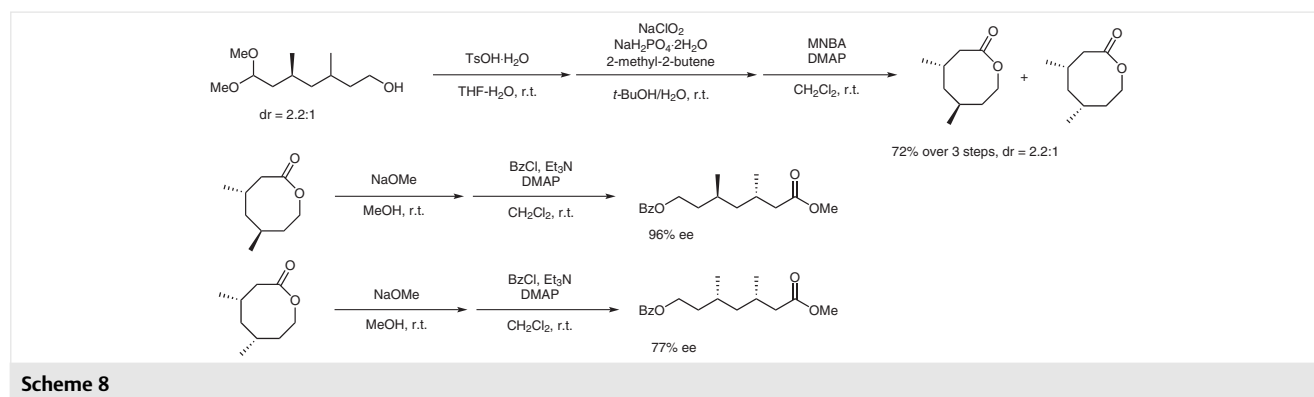
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### Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0037-1611644>.

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